

Air-Stable Ferrocene-Based Catholytes for Improved Performance in pH-Neutral Aqueous Organic Redox Flow Batteries

Bin Liu,[#] Manrong Song,[#] Yu Wang, Youke Chen, Honglin Chen, Jing Sun, Jiayou Ren, Xuan Shen, Xiacong Zhou, Chao Ji, Shengxin Yao, Liuping Chen, and Tianshou Zhao*Cite This: *J. Am. Chem. Soc.* 2025, 147, 30737–30746

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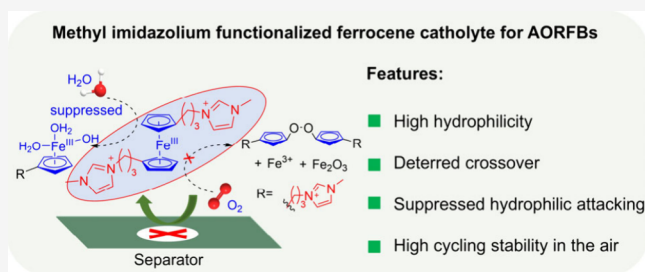


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ABSTRACT: Aqueous pH-neutral organic redox flow batteries are emerging as viable solutions for sustainable grid-scale energy storage. However, their advancement is hindered by the limited availability of catholytes that maintain stable cyclability in both ambient air and inert environments, as well as challenges related to low-cost synthesis and achieving high volumetric capacity. Here, we present the design and synthesis of a series of imidazolium-decorated ferrocene derivatives, culminating in the identification of an ionic liquid-like catholyte that sustains cycling stability in air for over 2000 cycles. At a concentration of 0.5 M, this catholyte exhibits remarkable cycling stability, with no capacity loss observed over a 68-day period in an inert atmosphere. Theoretical calculations and spectroscopic analyses reveal that the methyl imidazolium pendant group enhances compound stability and reduces hydrophilic attacks on ferrocenium through hydrogen-bonding interactions, thereby improving cycling stability. Notably, we have successfully constructed a pH-neutral stacked flow battery that achieves a peak power of 140 W and maintains an unprecedented capacity retention of 95% at 60 mA cm⁻² after 20,000 cycles. These findings not only introduce a novel pathway for developing highly stable catholytes but also facilitate assembling high-power-density stacked pH-neutral aqueous organic redox flow batteries.



INTRODUCTION

Large-scale stationary energy storage plays a significant role in modernizing the power grid through the integration of renewable energy sources into smart grids by balancing the mismatch between supply and demand, and enhancing grid resilience.^{1,2} Redox flow batteries (RFBs) are widely recognized as a reliable technology for large-scale energy storage because they store electrical energy in liquid electrolytes with different redox potentials, which are kept in external tanks that allow for the decoupling of energy and power.^{3–5} Vanadium RFBs (VRFBs) have been extensively researched due to their long lifetime and high safety, and are now commercially available.^{4,6} However, VRFBs suffer from issues such as electrolyte crossover, corrosive electrolyte, and the high cost of vanadium, which limit widespread adoption.^{7,8}

In recent years, redox-active organic and organometallic molecules have been widely adopted in aqueous organic RFBs (AORFBs) due to their high chemical diversity, natural abundance, and ease of structural modification.^{9–14} Various redox-active organic species, including quinones,^{15–17} pyridinium,^{18–23} metal ligand complexes,^{24,25} azobenzenes,^{26–28} nitroxide radicals,^{29–32} phenazines,^{33–35} and ferrocenes^{36–38} have been developed to achieve high volumetric capacity and high cycling stability in RFBs. Despite notable advances, designing cycling stable organic active species that are air-tolerant remains a critical challenge because the charged state

of redox active organic molecules can easily react with dissolved O₂, leading to the oxidation of electrolytes and irreversible side reactions such as nucleophilic attack, dimerization, and disproportionation, which contribute to the decay of battery capacity.^{18,39,40} An example of this is pyridinium species, which are highly sensitive to oxygen and can undergo significant decomposition due to nucleophilic attacks by hydroxide ions.^{18,40}

The research of air-tolerant electrolytes in AORFBs is in its infancy, with few redox active species having been explored.^{41–43} For example, Li et al. developed an air-stable methylene blue compound and demonstrated its practical application in a kW-scale stacked pH-acidic flow battery.⁴² They also synthesized stable air-tolerant naphthalene derivatives, which show no capacity decay over 40 days in an ambient atmosphere in acidic RFB tests.⁴¹ In recent years, pH-neutral AORFBs have gained significant research attention due to their noncorrosive nature and wider electrochemical stability window compared to pH-acidic or basic AORFBs.^{44,45} There

Received: March 26, 2025

Revised: August 4, 2025

Accepted: August 5, 2025

Published: August 12, 2025



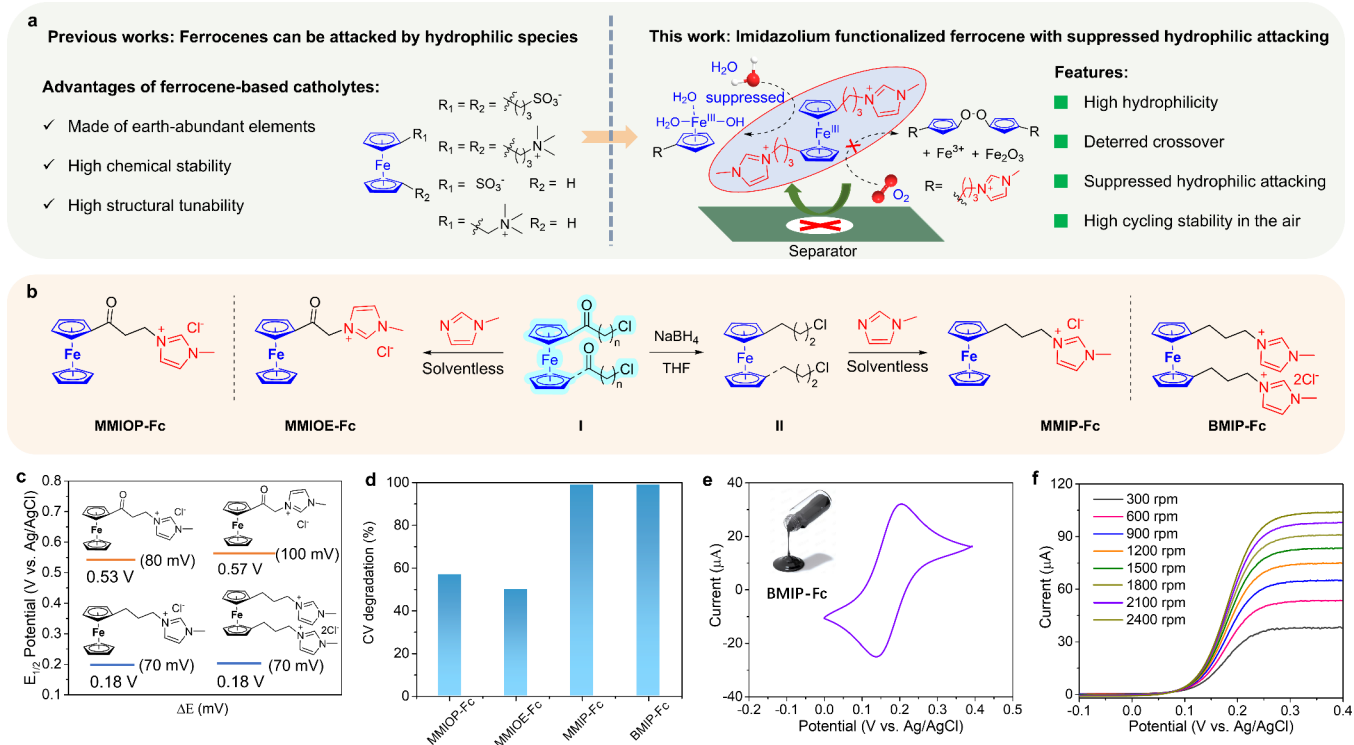


Figure 1. (a) Comparison of features between previously reported ferrocene-based catholytes and this work. (b) Molecular design and synthetic route of methyl imidazole-decorated ferrocene compounds. (c) Half-wave redox potentials and the difference between anodic and cathodic potential (ΔE) of the designed ferrocene compounds. (d) Degradation of the designed ferrocene compounds in cyclic voltammetry with repeated scans in a 0.5 M NaCl solution at 100 mV s⁻¹. (e) Cyclic voltammetry spectra of 2 mM BMIP-Fc in a 0.5 M NaCl solution at a scan rate of 100 mV s⁻¹. (f) Linear sweep voltammetry spectra of 1 mM BMIP-Fc in a 0.5 M NaCl solution at a scan rate of 5 mV s⁻¹.

is also interest in designing air-stable electrolytes; a rare example is the development of a class of bispyridinium electrolytes that enable stable operation in the air. However, to our knowledge, air-tolerant catholytes have not yet been studied in pH-neutral AORFBs, even though equally important for developing air-tolerant full RFB systems. More importantly, despite significant progress made in developing catholytes in pH-neutral AORFBs with certain advantages, catholytes that combine the advantages of high cycling stability in ambient and inert atmospheres, low-cost synthesis, and high cycling stability at high volumetric capacity remain unavailable. This presents a critical challenge in developing stable, high-power stack-level pH-neutral AORFBs. Demonstrating pH-neutral AORFB in a stacked battery (e.g., > 100 W scale), similar to what is done with pH-acidic AORFBs, is crucial, as it helps to avoid potential issues that might not be observed in lab-scale single-cell tests and validate the practical large-scale implementation of pH-neutral AORFB technology.

In this paper, we report the rational design and synthesis of a class of methyl imidazolium-functionalized ferrocenes for pH-neutral AORFBs. Fundamental physicochemical and electrochemical investigations led to the identification of an air-stable, ionic liquid-like catholyte, 3,3'-(1,1'-ferrocenediyl-di-4,1-propanediyl)bis[1-methyl-1H-imidazolium] chloride (BMIP-Fc), which can be cycled for 2000 cycles under an air atmosphere without detectable oxygen-related molecular degradation. An assembled full RFB with a 0.5 M catholyte concentration can be cycled for 2,000 cycles (68 days) in an inert atmosphere without capacity loss, representing one of the most stable AORFBs reported. Theoretical calculations and spectral experiments reveal that the methyl imidazolium

pendant enables high chemical stability of the compound and mitigates hydrophilic attacks on ferrocenium through hydrogen bond effects, thus improving cycling stability under air and inert atmosphere. Notably, the first pH-neutral stacked AORFB was constructed, demonstrating a peak power of 140 W and an unprecedented capacity retention of 95% at 60 mA cm⁻² after 20,000 cycles.

RESULTS AND DISCUSSION

Among various catholytes, ferrocene derivatives functionalized with quaternary ammonium,^{39,40,46} bipyridinium ammonium,⁴⁷ and sulfonate groups have been widely applied in pH-neutral AORFBs.^{37,48} However, ligand dissociation reactions resulting from nucleophilic attacks occurred during cycling.^{37,48} To develop robust, more cycling-stable ferrocene-based catholytes, we initially reasoned that the aromatic characteristics of methyl imidazolium facilitate the overlap of p-orbitals and enhance intermolecular interactions. This could improve the chemical and electrochemical stability of the catholytes, thereby achieving high cyclability in the RFB tests. Furthermore, imidazolium cations can pair with anions to form highly water-soluble salts that exhibit ionic liquid properties, resulting in high volumetric capacity. Consequently, we propose the design of a series of ferrocene compounds incorporating various methyl imidazolium pendants (Figure 1b). We designed the ferrocenes MMIOP-Fc and MMIOE-Fc, which feature a strong carbonyl (C=O) electron-withdrawing group positioned between the imidazolium and the ferrocene moiety, aiming to achieve a high redox potential. Additionally, we synthesized the compounds MMIP-Fc and BMIP-Fc, which do not contain the C=O group. All compounds undergo Friedel–Crafts

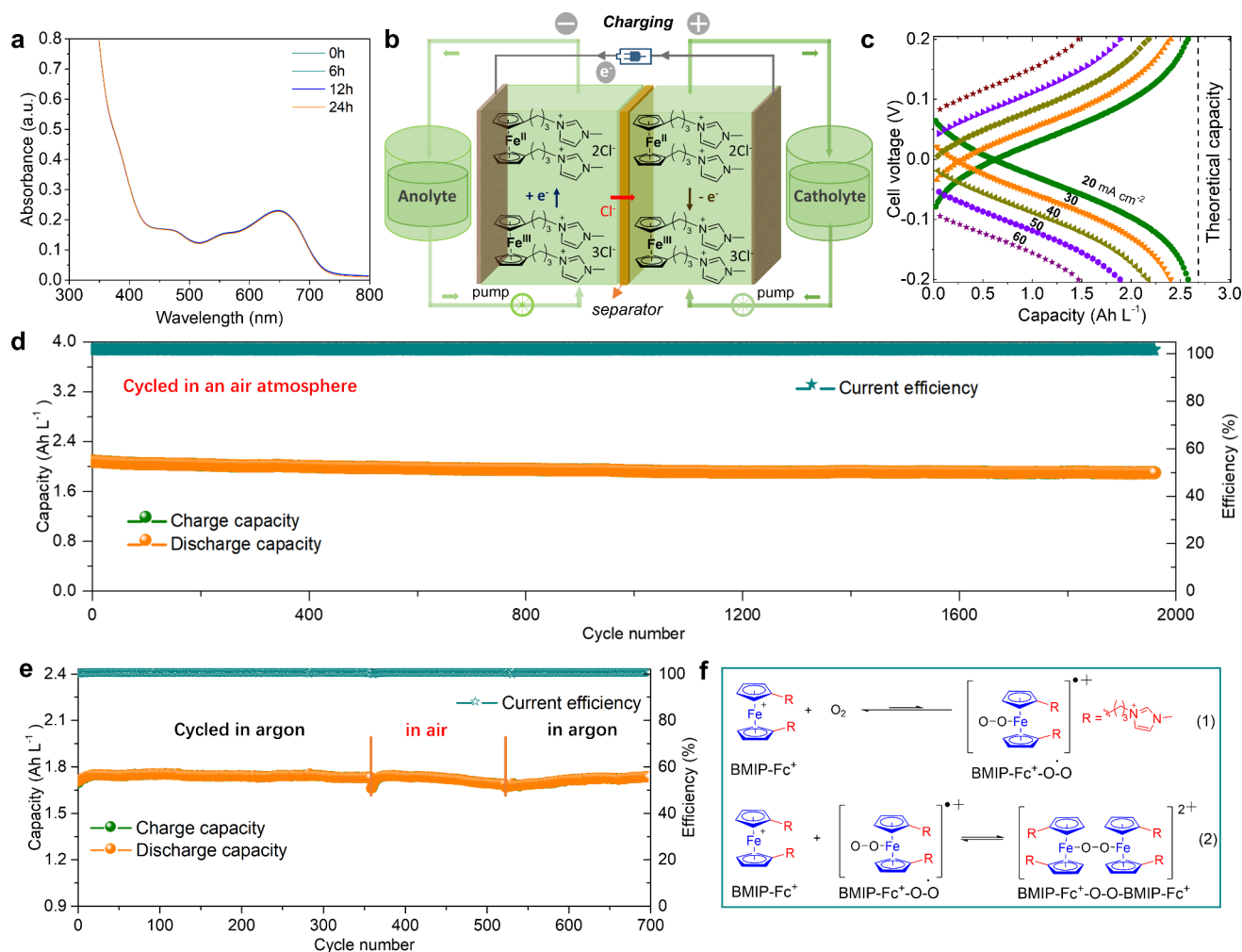


Figure 2. (a) UV-vis stability studies of the charged 2 mM BMIP-Fc catholytes under an air atmosphere for 24 h. (b) Schematic representation of the BMIP-Fc symmetric flow cell during charging. (c) Representative charge-discharge curves of the 0.1 M BMIP-Fc symmetric flow cell from 20 to 60 mA cm⁻² in an air atmosphere. (d) Charge/discharge capacity and current efficiency of the 0.1 M BMIP-Fc symmetric RFB over 2,000 cycles at 50 mA cm⁻². (e) Charge/discharge capacity and current efficiency variation of the 0.1 M BMIP-Fc symmetric RFB in argon, in air, and again in argon. (f) The proposed radical coupling reaction occurs at the iron center, resulting in a μ-peroxy iron radical cation and/or a μ-peroxy di-iron complex.

alkylation of ferrocene. The treatment of monosubstituted alkylated ferrocene with methyl imidazole yields the compounds MMIOP-Fc and MMIOE-Fc, while MMIP-Fc and BMIP-Fc are obtained by reacting methyl imidazole with NaBH₄-reduced alkylated ferrocenes. The density functional theory (DFT) modeling of the local charge distribution of MMIOP-Fc, MMIP-Fc, and BMIP-Fc shows a distinct separation of electron-dense and electron-deficient regions, suggesting strong interactions with solvent water molecules (Figure S1). MMIOP-Fc and MMIOE-Fc exhibit similar solubilities of 1.88 mol L⁻¹ and 1.68 mol L⁻¹, respectively (Figures S2–S3). In contrast, MMIP-Fc and BMIP-Fc exhibit ionic liquid-like properties, appearing as a viscous, asphalt-like liquid (Figure S4), which makes them highly miscible with aqueous solution. Notably, BMIP-Fc demonstrates a high solubility of 3.2 mol L⁻¹ in a 1.0 mol L⁻¹ NaCl solution. The initial electrochemical properties of the compounds were assessed via cyclic voltammetry (CV) measurements, revealing E_{1/2} values of 0.53 V, 0.57 V, 0.18 V, and 0.18 V vs. Ag/AgCl (Figure 1c and 1e), corresponding to the Fe²⁺/Fe³⁺ redox reactions. Despite their high redox potential, MMIOP-Fc and

MMIOE-Fc exhibit inferior electrochemical stability when scanned 100 times (Figure S6). This instability is attributed to increased nucleophilic attack resulting from the strong electron-withdrawing effect of the C=O group on the electron-deficient Fe³⁺ in ferrocene, making these compounds unstable in the cycling tests.⁴⁹ In contrast, MMIP-Fc and BMIP-Fc remained stable when scanned for 200 cycles (Figure 1d and S5). The double-substituted imidazolium ferrocene BMIP-Fc has a larger molecular size than MMIP-Fc, and its doubled charge can help reduce species crossover.⁴⁰ Therefore, BMIP-Fc was selected as the model compound for further RFB tests. The electrochemical properties of BMIP-Fc were further studied using linear sweep voltammetry (LSV) (Figure 1f), which corresponded to a diffusion coefficient (*D*) of 4.12 × 10⁻⁶ cm² s⁻¹. Based on the Levich equation and Tafel plot, the electron-transfer rate constant (*k*₀) was determined to be 1.27 × 10⁻² cm s⁻¹ (Figure S7), which was comparable to those of previously reported redox-active species.^{33,44} The fundamental chemical stability of BMIP-Fc under aqueous conditions was evaluated via ¹H NMR (Figure S8). The compound was exposed to air for 10 days and did not exhibit any structural

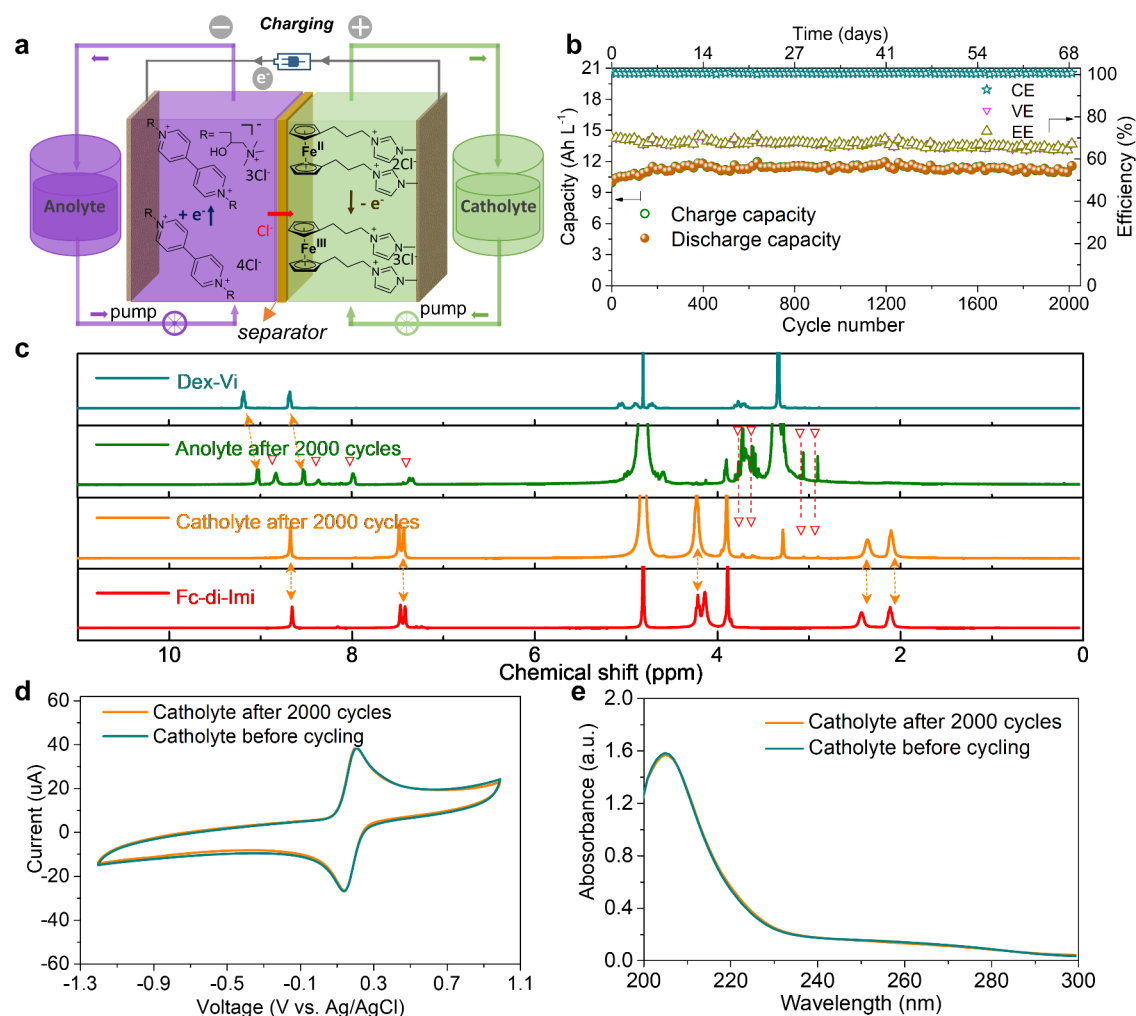


Figure 3. (a) Cell structural configuration and anodic/cathodic redox reactions of the BMIP-Fc/Dex-Vi RFB. (b) Charge/discharge capacity, CE, EE, and VE over 2,000 cycles at 40 mA cm^{-2} . (c) Comparison of the ^1H NMR spectra of the electrolytes before and after 2,000 cycles (new signals are marked with red inverted triangles, and the signal of the anolyte or catholyte is marked with yellow arrows). (d) Comparison of the CV spectra of the catholyte before and after 2,000 cycles.

changes. Its structure remained stable even after being stored in an aqueous solution for 30 days, at 50°C for 13 days, and in the charged state for 24 h at 50°C , demonstrating its high stability.

The high chemical stability of BMIP-Fc encouraged us to investigate its stability in the presence of O_2 in its charged state. The obtained BMIP-Fc $^+$ electrolyte solution was a yellow-green liquid that maintained its color for an extended period when exposed to air. Then, a diluted charged solution (BMIP-Fc $^+$) was prepared, and the absorbance was recorded using UV-vis spectroscopy. As shown in Figure 2a, after 24 h, the absorbance of the electrolyte remained almost identical to that of the original electrolyte solution, further confirming the high stability of the charged BMIP-Fc $^+$ solution in an air atmosphere. This prompted us to conduct charge/discharge battery tests to assess the cycling stability of BMIP-Fc in an air atmosphere. As shown in Figure 2b, a symmetric RFB was assembled and the electrolytes on both sides were alternated between BMIP-Fc and BMIP-Fc $^+$. The initial cycling tests of the RFB involved a rate study to examine how the accessed capacity varies with increasing current density. Figure 2c shows the accessed charge and discharge capacities as a function of potential. During constant current cycling at 20, 30, 40, 50, and

60 mA cm^{-2} , the accessed capacities were 96.2%, 89.6%, 81.3%, 70.9%, and 55.2% of the theoretical capacity (2.68 Ah L^{-1}), respectively. The accessed capacity decreases with increasing current density due to higher cell polarization. Based on the rate study, a current density of 50 mA cm^{-2} was selected to evaluate the long-term cycling stability. Figure 2d presents the charge and discharge capacities, along with the current efficiencies, as a function of the cycle number. The mean accessed capacity is approximately 70% of the theoretical value. The symmetric RFB exhibited a stable current efficiency of $100\% \pm 0.04$ and 95% capacity retention over 2,000 cycles, demonstrating its high cycling stability in an air atmosphere. To gain a more in-depth understanding, a supplementary test was conducted. In this test, the cells were first galvanostatically cycled 360 times under argon. Following this, the electrolyte solutions were sparged, exposed to air, and cycled for an additional 165 times. Subsequently, the solutions were sparged again with argon and cycled a final 175 times. As shown in Figure 2e, the battery maintained stable capacity retention when cycled in an argon atmosphere. When exposed to and sparged with air, the capacity initially increased as the electrolyte required some time to reach equilibrium after the test began. However, it slightly decreased with continued

cycling in the air. The minor capacity drop in the air atmosphere is unlikely to result from the irreversible decomposition of ferrocenium molecules, which produce Fe^{3+} or Fe_2O_3 due to the influence of O_2 . This deduction can be supported by the postcycling HR-MS, CV, and ^1H NMR analysis of the cycled anolyte and catholyte in the air atmosphere, which showed that the electrolytes remained stable during cycling and no signals for any possible dioxygen-decomposition species in the HR-MS spectra (Figure S9 and S10). The finding contrasts with previous proposals that two ferroceniums can react with an oxygen molecule to form an unstable dimeric complex with an $-\text{O}-\text{O}-$ bridge, which decomposes to Fe_2O_3 , cyclopentadienyl peroxide, and Fe^{3+} through the nucleophilic attack of water and oxygen.^{50,51} Since the capacity recovered and stabilized when cycled again in an argon atmosphere, the radical coupling reaction likely occurs at the iron center, reversibly forming a μ -peroxy iron radical cation ($\text{BMIP-Fc}^+-\text{OO}^-$) and/or a μ -peroxo di-iron complex ($\text{BMIP-Fc}^+-\text{OO-Fc}^+-\text{BMIP}$).^{52,53} The μ -peroxo di-iron complexes remain stable as intermediates in an air atmosphere and can convert to ($\text{BMIP-Fc}^+-\text{OO}^-$) and BMIP-Fc^+ when O_2 is removed (Figure 2f). Additionally, an asymmetric full flow battery using BMIP-Fc as the catholyte and air-stable $[(\text{NPr})_2\text{PV}]\text{Cl}_4$ as the anolyte was assembled to assess the cycling stability in an air atmosphere. The battery demonstrated moderate cycling stability in the air, with a capacity decay of 40% after 220 cycles (Figure S11). Post-mortem analysis of the cycled electrolyte indicated that the capacity decay is primarily attributed to the air instability of the anolyte, which decomposes during the cycling tests.¹⁸ BMIP-Fc showed no chemical degradation (Figure S12). To sufficiently assess the air cycling stability of BMIP-Fc in the asymmetric full flow battery, it is essential to develop robust air-stable anolytes that are more stable and can be cycled for a longer cycle lifetime. In conclusion, BMIP-Fc exhibits high cyclability in air atmospheres in symmetric RFBs and shows no chemical degradation in asymmetric RFBs, validating its applicability as an air-tolerant catholyte in pH-neutral AORFBs. BMIP-Fc represents the first air-tolerant catholytes reported in pH-neutral AORFBs.

The cycling performance of BMIP-Fc in an inert atmosphere was also explored to gain further insights into the cycling stability. In pH-neutral RFBs, demonstrating high cycling stability of active species at elevated concentrations remains challenging, as limited species have shown a long lifetime (e.g., ≥ 2000 cycles and ≥ 30 days) with a reasonably high electrolyte concentration (≥ 0.5 M). For the anolyte of the flow battery, Dex-Vi is used due to its high cycling stability and low-cost synthesis (Figure 3a).²¹ It has a lab-scale synthesis price of US \$0.30 g^{-1} , significantly lower than the cost of $[(\text{NPr})_2\text{PV}]\cdot 4\text{Cl}$ at US\$21.22 g^{-1} (Table S1).^{21,32} The battery was initially tested with 0.1 and 0.5 M BMIP-Fc active species, demonstrating remarkably stable capacity retention. Detailed information on the battery performance with the 0.1 M electrolyte concentration and decomposition analysis can be found in Figures S13–S17. The performance of the battery at a 0.5 M electrolyte concentration, corresponding to a theoretical capacity of 13.4 Ah L^{-1} , is presented in Figure 3b. Following the rate study (Figure S18), long-term cycling performance was assessed at a current density of 40 mA cm^{-2} . The RFB exhibited a stable energy efficiency (EE) of approximately 68% $\pm$ 0.3%, a Coulombic efficiency (CE) of 99% $\pm$ 0.04%, and a voltage efficiency (VE) of 68% $\pm$ 0.04%. No capacity fading

was observed over 2,000 cycles (68 days), making it one of the most stable RFBs among pH-neutral AORFBs reported (Table S2), despite slight capacity fluctuations induced by temperature changes. Post-mortem characterization (^1H NMR, CV, and UV–vis) of cycled BMIP-Fc revealed no detectable structural degradation, as evidenced by the absence of new signals in these spectra (Figure 3c–e). These results qualitatively demonstrate the inherent chemical stability of BMIP-Fc during the cycling test. However, CV, ^1H NMR, and HR-MS analyses revealed that the Dex-Vi anolyte underwent inevitable molecular decay and produced monosubstituted species and the dextrosil pendant (Figure S19). Notably, no crossover of BMIP-Fc species was detected on the anode side by CV and ^1H NMR, indicating ultralow permeability across the DSVn membrane. This is consistent with the low permeability of BMIP-Fc, which was calculated to be $7.33 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ (Figure S20). To demonstrate the highest volumetric capacity among ferrocene-based catholytes, the battery performance was evaluated with a 1.8 M electrolyte concentration (theoretical volumetric capacity of 48.24 Ah L^{-1}). The high viscosity of the 1.8 M solution did not restrict the rate performance of the battery, as a high-capacity utilization rate of approximately 96% was achieved at a current density of 20 mA cm^{-2} (Figures S21–S23). Remarkably, this capacity is recorded at the highest reported concentration for ferrocene-based organic cathode species in neutral aqueous solutions. Post-mortem electrolyte analysis of the 1.8 M cell after cycling using ^1H NMR, CV, UV–vis, and HR-MS indicated that no apparent chemical or electrochemical degradation of the BMIP-Fc catholyte was detected, verifying its high stability (Figures S24–S26). The RFB retained approximately 80% of its capacity after being cycled for 640 cycles (66 days), corresponding to a capacity decay rate of 0.3% per day, demonstrating the superior cycling stability of the catholyte. However, monobipyridine-dex and dextrosil decayed from the Dex-Vi and were detected on both the anode and cathode sides, similar to low-concentration RFBs. The capacity decay of the battery is inferred to be predominantly caused by anolyte decay, minor electrolyte leakage, and minimal catholyte crossover (Figures S26–S28).

The large size and charge repulsion of the methyl imidazolium group could be important factors contributing to the unexpectedly high cycling stability of BMIP-Fc under air and argon atmospheres. However, investigating the underlying mechanism by which the imidazolium group influences the stability of ferrocene catholytes is essential for gaining deeper insights. We further examined the stability of MMIOP-Fc and MMIOE-Fc to elucidate their degradation mechanisms. ^1H NMR analysis indicates that both MMIOP-Fc and MMIOE-Fc undergo structural decomposition when stored at 50 $^\circ\text{C}$ for more than 1 week, demonstrating inferior chemical stability compared to BMIP-Fc (Figure S29). Importantly, EPR, ^1H NMR, and HR-MS analyses of the cycled electrolyte confirmed significant decomposition of these compounds and the identification of the decomposed free ligand (Figures S30–S33). This finding supports our previous proposal that the presence of strong electron-withdrawing $\text{C}=\text{O}$ groups renders the iron center susceptible to attack by nucleophilic species. Furthermore, we performed a more in-depth analysis of the charge distribution in the BMIP-Fc, MMIOP-Fc, and MMIOE-Fc molecules using DFT calculations combined with atomic population analysis. As shown in Figure S34, calculations were performed for both Fe(III) and Fe(II) oxidation states for each

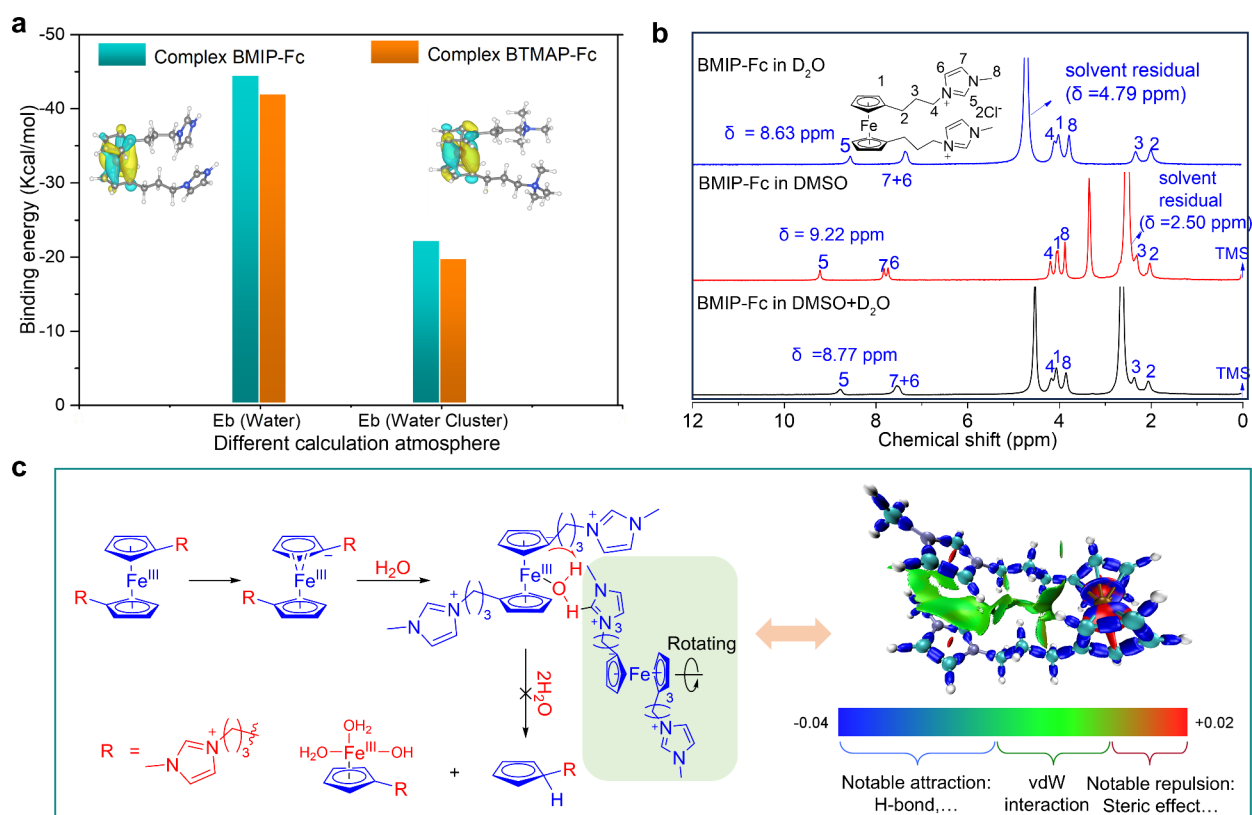


Figure 4. (a) Binding energy of BMIP-Fc and BTMAP-Fc in different calculation atmospheres of water and water clusters. (b) ¹H NMR spectra of 20 mM BMIP-Fc in D₂O, DMSO, and 1:1 (v/v) D₂O/DMSO mixtures, with the hydrogen atoms in the molecular structure correlated to their corresponding chemical shifts in the NMR spectra. (c) The proposed mechanism illustrates the beneficial effects of hydrogen bonds from the imidazole pendant in preventing H₂O from attacking BMIP-Fc⁺ during cycling and IRI showing the surface map of BMIP-Fc. The red, green, blue, and white balls represent the oxygen, carbon, nitrogen, and hydrogen atoms, respectively. The blue bars and regions bridging the atoms represent chemical bonds. The green region represents the van der Waals force (vdW). The red region represents repulsion.

of these three molecules. The Hirshfeld atomic charge on the Fe center was found to be higher in the Fe(III) state than in the Fe(II) state for all molecules. A higher Hirshfeld atomic charge reflects a greater susceptibility to nucleophilic attack, thus rendering the Fe(III) species less stable. Additionally, we observed that for both Fe(II) and Fe(III) states, the Fe atoms in MMIOP-Fc and MMIOE-Fc exhibit higher Hirshfeld atomic charges compared to BMIP-Fc. This indicates that the Fe centers in MMIOP-Fc and MMIOE-Fc are more prone to nucleophilic attack than the Fe center in BMIP-Fc. A trade-off between stability and redox potential persists, which should be carefully considered when designing high-redox-potential ferrocene-based catholytes.

Besides, we compared the Gibbs free energy changes in the binding processes of BMIP-Fc and BTMAP-Fc (Figure S35). The results indicate that the binding of BMIP-Fc, involving 3-(3-(cyclopenta-3,5-dien-2-ylidene-1-yl)propyl)-1-methyl-1H-imidazol-3-ium and Fe^{II}(H₂O)₆, is more stable, as indicated by the lower binding energy in both the water and water cluster simulation atmospheres (Figure 4a). Importantly, the experimental results are consistent with the DFT calculation result, as the capacity decay of the 0.1 M BTMAP-Fc/Dex-Vi RFB exhibits a higher rate than that of the 0.1 M BMIP-Fc/Dex-Vi RFB (Figure S36). We also investigate whether the aromatic methyl imidazole group promotes intermolecular interactions. DFT optimization calculations reveal that the angles between the planar structure of the aromatic methylimidazole five-membered ring and other aromatic planar rings range from

61.4° to 67.6°, indicating that they are far from parallel. Furthermore, the closest approach distance between these molecules reaches 4.52 Å (Figure S37). This combination of a large twist angle and a separation distance well beyond the typical range for effective π -orbital overlap effectively precludes the formation of significant intermolecular π - π bonding. This finding aligns with prior similar studies, which noted that no π -stacking interactions were observed between the imidazolium ring of the solvent cation and the cyclopentadienyl motif of ferrocene.⁵⁴ The high cycling stability of BMIP-Fc is proposed to originate from hydrogen bond interactions involving three hydrogen atoms on the imidazolium ring. The hydrogen atoms of the imidazolium ring could interact with H₂O through hydrogen bond interactions, which prevents the formation of R-cyclopenta-Fe³⁺(H₂O)₂(OH) species and cyclopenta-R-H, thereby suppressing the decomposition of the BMIP-Fc⁺ species (Figure 4C).³⁹ The presence of hydrogen bond interactions was confirmed by ¹H NMR spectroscopy experiments. As illustrated in Figure 4b, the protons on the imidazolium group of BMIP-Fc in DMSO exhibited increased chemical shifts compared to those in DMSO/D₂O mixtures and D₂O, indicating strong hydrogen bond interactions between the three proton atoms of -CH and a strong hydrogen bond acceptor (S = O).^{54,55} In contrast, control experiments using a nonimidazolium analogue, BTMAP-Fc, demonstrated that the protons of the trimethylammonium group (-N(CH₃)₃⁺) showed no significant changes in chemical shifts ($\Delta\delta < 0.01$ ppm). (Figure S38). The

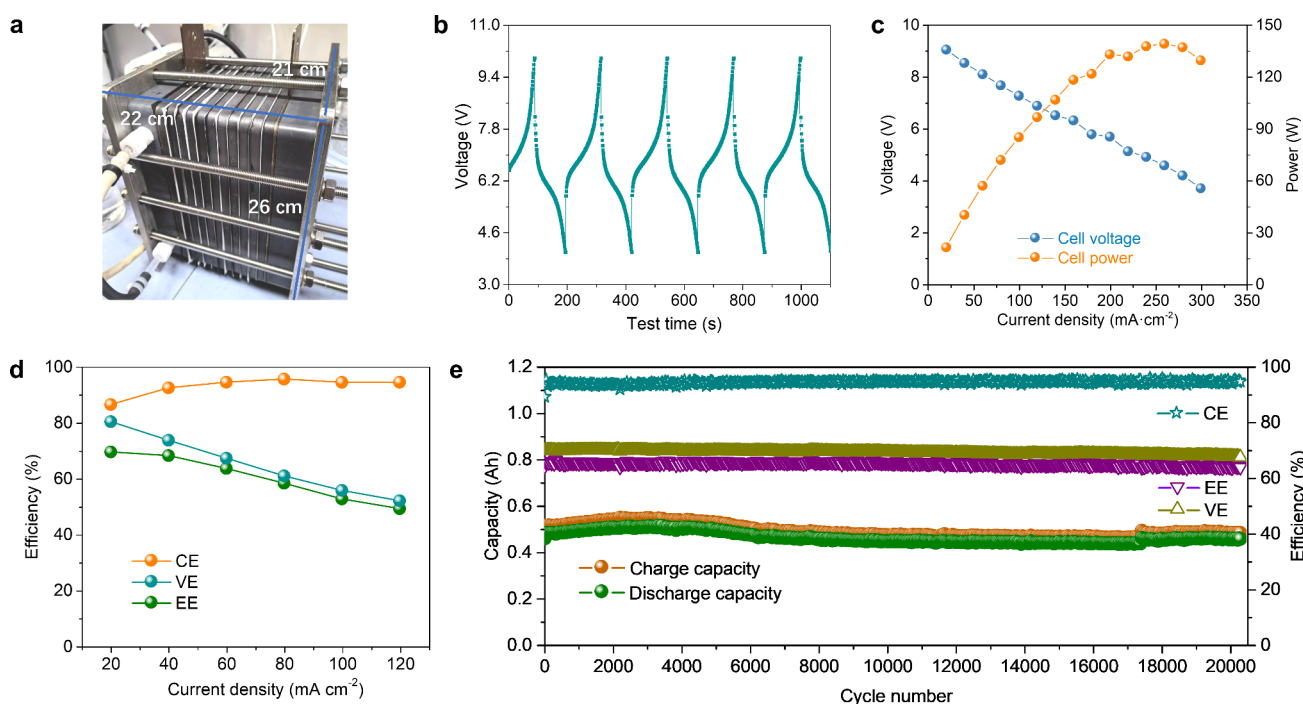


Figure 5. (a) BMIP-Fc/Dex-Vi stacked RFB with 10 single cells. (b) Representative charge–discharge curves of the battery's first five cycles. (c) Polarization curves and cell power of the Dex-Vi/BMIP-Fc stacked RFB. (d) CE, EE, and VE of the Dex-Vi/BMIP-Fc stacked RFB at current densities of 20–120 mA cm^{−2} with an increment of 20 and 150 mA cm^{−2}. (e) Charge/discharge capacity, CE, EE, and VE over 20,000 cycles at 60 mA cm^{−2}.

intermolecular hydrogen bond interactions of BMIP-Fc were further investigated through the interaction region indicator (IRI) and visualized using Multiwfn.⁵⁶ The IRI visualization revealed intricate networks of covalent bonding and weak noncovalent interactions (e.g., van der Waals forces (vdW), hydrogen bond effects) (Figure 4c). These combined analyses suggest that competing interactions prevent the attack of H₂O on the Fe³⁺ center of ferrocenium, thereby contributing to the exceptional cycling stability of BMIP-Fc.

Importantly, the ultrastable electrochemical and cycling performance, along with the easy, and low-cost kilogram-scale synthesis of BMIP-Fc, have motivated us to construct a 100-W scale stacked RFB to evaluate the practical scale-up application of the catholyte in pH-neutral AORFBs. We found that BMIP-Fc could be synthesized at \$0.53/g at the lab scale, benefiting from an overall high synthetic yield of 84% and \$19.75/kg at a 1 t (MT) scale (Table S3–S4). For comparison, the cost of synthesizing BTMAP-Fc (Table S5) and N+TEMPOD (Table S6) at the lab scale is \$1.64/g and \$5.66/g, respectively, both of which are substantially higher than that of BMIP-Fc. Thus, BMIP-Fc demonstrates a remarkable cost advantage compared with commonly used catholytes, representing its promise for grid-scale energy storage applications. For the first time, a stacked battery with 10 flow units, each with an area of 117 cm², was assembled (Figure 5a). This stacked RFB demonstrated distinct charge/discharge plateaus in the tests (Figure 5b). The polarization curves indicated that the instantaneous discharge power of the stack batteries can reach 140 W at a current density of 260 mA cm^{−2} (Figure 5c). As shown in Figure 5d and Table S8, the stacked battery exhibited CEs of 86.9%, 91.4%, 93.7%, 94.7%, 96.1%, 96.3%, and EEs of 78.6%, 75.2%, 69.5%, 64.0%, 58.6%, 53.6%, at the current densities of 20, 40, 60, 80, 100, and 120 mA cm^{−2}, respectively, agreeing well with the low resistance of the

battery (Figure S40). The battery maintained a stable long-period cycle at 60 mA cm^{−2} for over 20,000 cycles with around 95% capacity retention (Figure 5e), and no new ¹H NMR signals of the BMIP-Fc catholyte were observed after cycling (Figure S41). Notably, we also assembled a stacked battery with a high capacity of 4.0 Ah (using a 1.8 M electrolyte concentration). The battery was cycled for 260 cycles (~200 h) without significant capacity fade, demonstrating the high cycling stability of BMIP-Fc in the stacked battery (Figure S42). To the best of our knowledge, this is the first stacked battery reported in a pH-neutral AORFB, indicating that aqueous pH-neutral ORFB with ferrocene catholyte is a viable candidate for developing large-scale AORFBs.

CONCLUSIONS

In conclusion, we designed and synthesized a class of imidazolium-functionalized ferrocenes. The BMIP-Fc catholyte, which exhibits high chemical stability, low permeability, and cost-effective synthesis, was employed in pH-neutral AORFBs. This catholyte can be cycled stably in the RFB under air for 2,000 cycles without detectable oxygen-related molecular degradation. The full RFB with a 0.5 M active electrolyte could be cycled for 2,000 cycles (68 days) without capacity fading. At a high electrolyte concentration of 1.8 M, the flow battery was cycled for 66 days without detectable molecular degradation. Theoretical calculations and spectral experiments reveal that the incorporation of the methyl imidazolium group improves compound stability and prevents hydrophilic attack on ferrocenium via hydrogen bonding effects, thereby allowing for high cycling stability under both air and inert atmospheres. Importantly, a pH-neutral stacked RFB was constructed, demonstrating a peak power of up to 140 W and an unprecedented capacity retention of 95% at 60 mA cm^{−2} after 20,000 cycles. These results present a novel

approach to developing highly air-stable catholytes and pave the way for fabricating high-power-density stacked pH-neutral AORFBs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c05219>.

Detailed synthetic procedures and characterization data; solubility measurements; comprehensive electrochemical analysis (CV, LSV, EIS); theoretical DFT calculations; supplementary figures ($^1\text{H}/^{13}\text{C}$ NMR spectra, UV–vis spectra, cycling performance plots); additional tables (cycling performance data, cost analysis) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Tianshou Zhao – Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong SAR 999077, China; Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China; orcid.org/0000-0003-4825-2381; Email: zhaots@sustech.edu.cn

Authors

Bin Liu – Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong SAR 999077, China

Manrong Song – Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Yu Wang – Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong SAR 999077, China; orcid.org/0000-0002-2972-3486

Youke Chen – Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Honglin Chen – Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Jing Sun – Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong SAR 999077, China; orcid.org/0000-0001-9277-9047

Jiayou Ren – Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong SAR 999077, China

Xuan Shen – Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Xiacong Zhou – Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Chao Ji – Jiangsu Engineering Research Center for Comprehensive Utilization of Well and Rocks Salt, Chinasalt Jintan Co., Ltd., and China Salt Cavern Comprehensive Utilization Co., Ltd., Changzhou 213200, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China; orcid.org/0000-0001-6084-0712

Shengxin Yao – Jiangsu Engineering Research Center for Comprehensive Utilization of Well and Rocks Salt, Chinasalt Jintan Co., Ltd., and China Salt Cavern Comprehensive Utilization Co., Ltd., Changzhou 213200, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Liuping Chen – Jiangsu Engineering Research Center for Comprehensive Utilization of Well and Rocks Salt, Chinasalt Jintan Co., Ltd., and China Salt Cavern Comprehensive Utilization Co., Ltd., Changzhou 213200, China; Joint Research Center on Energy Storage Technology in Salt Caverns, Shenzhen 518055, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.5c05219>

Author Contributions

[#]B. Liu and M.R. Song contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

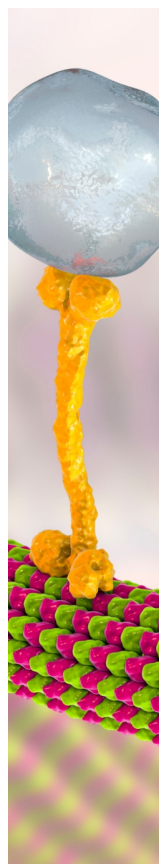
The work described in this paper was supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region, China (T23-601/17-R), and the Guangdong Major Project of Basic and Applied Basic Research (2023B0303000002).

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